Flame retardant nanocomposites with layer double hydroxides

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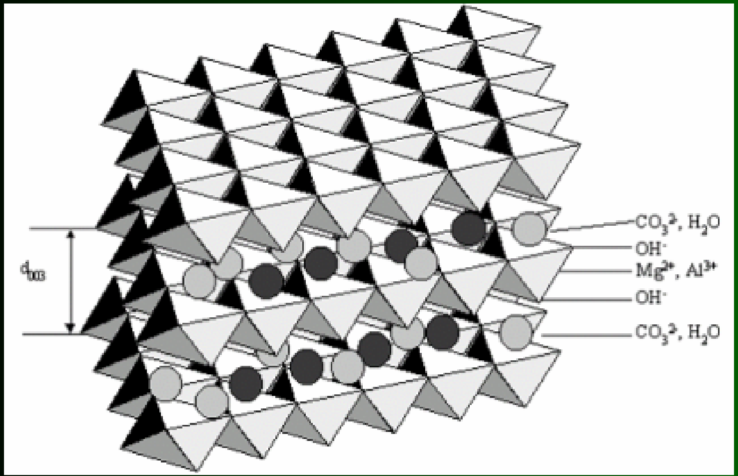
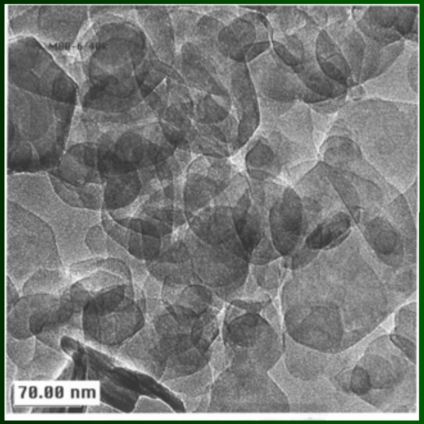
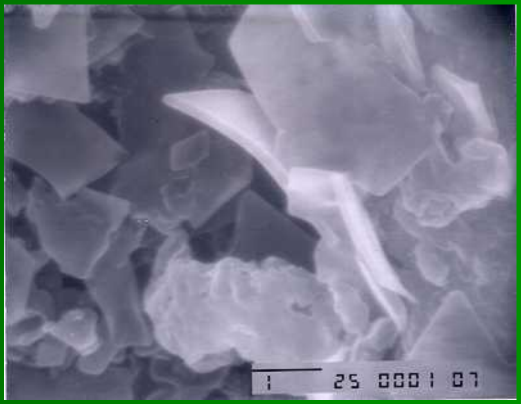
LDH



- LDH are similar to brucite, $Mg(OH)_2$ are anionic clays of the formula $[M^{(II)}_{1-x}M^{(III)}_x(OH)_2]^{x+}[A^{m-}]_{x/m}\bullet 2H2O]^{x-}$, where A^{m-} is any of a large range of anions such as CO^{2-}, Cl^-, carboxylates, sulfates or sulfonates.
- Conventionally synthesized LDH's are strongly hydrophilic materials, either amorphous or microcrystalline with hexagonal habit, with the dominant faces developed parallel to the metal hydroxide layers.
- Adjacent layers are tightly bound to each other

Properties of LDH

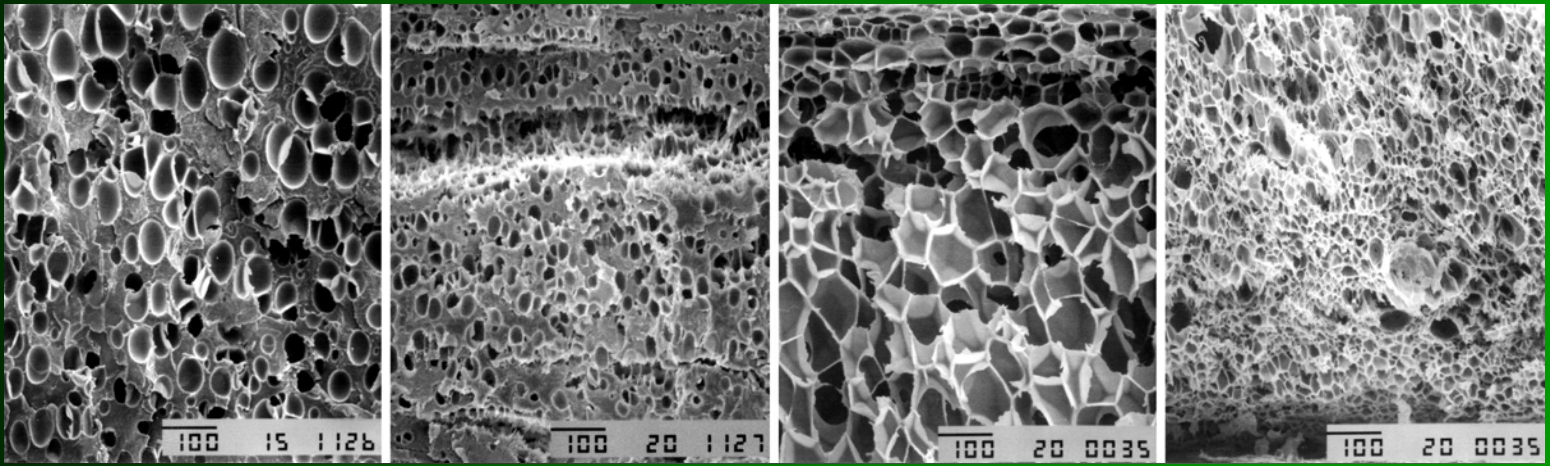




- Highly surface active, uniform size and shape synthetic nanofillers with 3 active sites per nm^2
- Functionalization can be tailored to release water and CO_2
- Chemistry can be tailored to enhance char formation

Supercritical CO2 Reactor

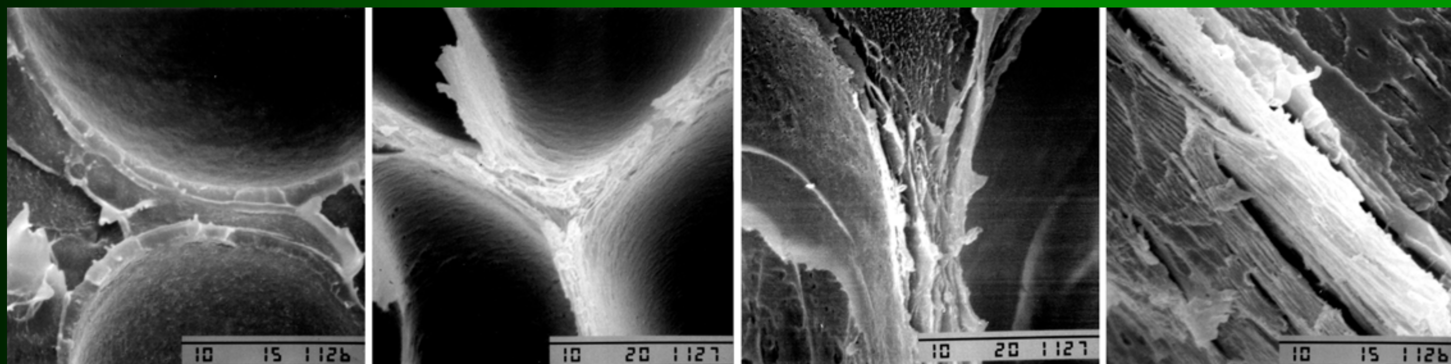
Results: MLS concentration



a b c d

- SEM Micrographs (100X magnification) showing that effect of MLS concentration on cell density (N_f).[a] Pure PS, 60°C, [b] 1%MLS, 60°C, [c] 1%MLS, 85°C, [d] 3%MLS, 85°C
- Increased concentration of clay led to increased nucleation sites

Where does the clay lie?



a b c d

- SEM micrographs (5000X magnification) showing aligned grain structure in nanocomposite cell walls. [a] Pure PS (no visible alignment), 60°C, [b] 1%MLS, 60°C, [c] 1%MLS, 85°C, [d] 1%MLS, 75°C
- Clay presence in the foam walls produces a striated cell wall of non-circular shape

Compared to Montmorillonite layered silicates

- LDH have high charge density. The charge density is dependent on the metal ratio. A lower divalent:trivalent ratio, the higher the charge density. More trivalent metal, more positive charge. For example: a 2:1 M(II)/M(III) LDH would have a higher charge density than a 3:1 M(II)/M(III) LDH.
- Anions exposed by exfoliation have less exothermic solvation energies than the cations exposed by smectite exfoliation.
- LDH exfoliation has therefore been a challenge

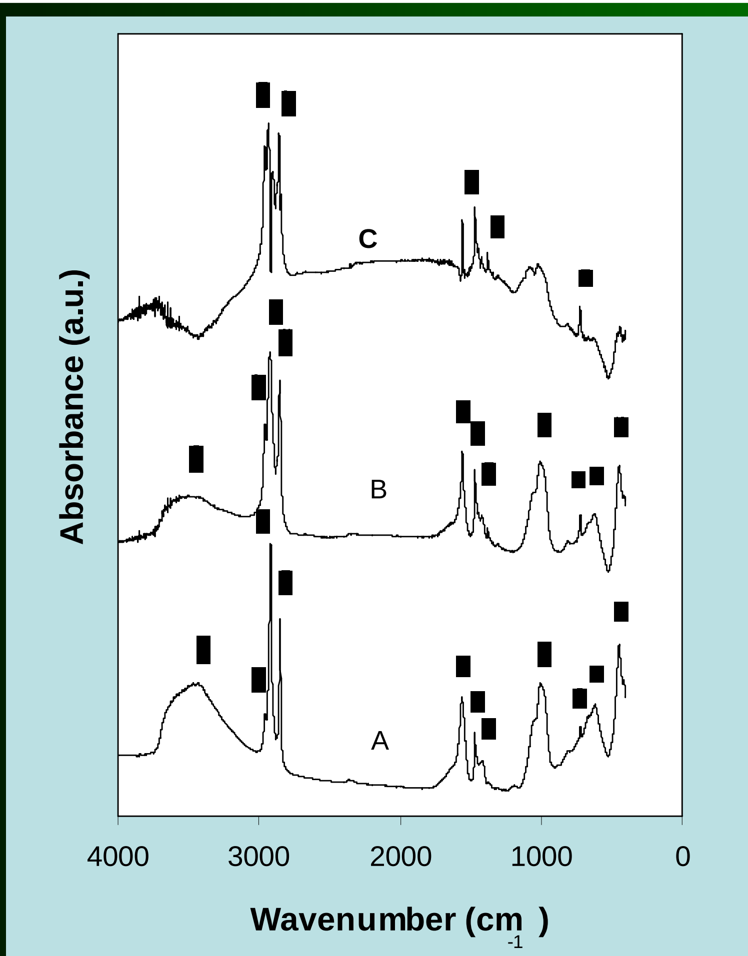
Chemistry and Polymer Engineering approaches

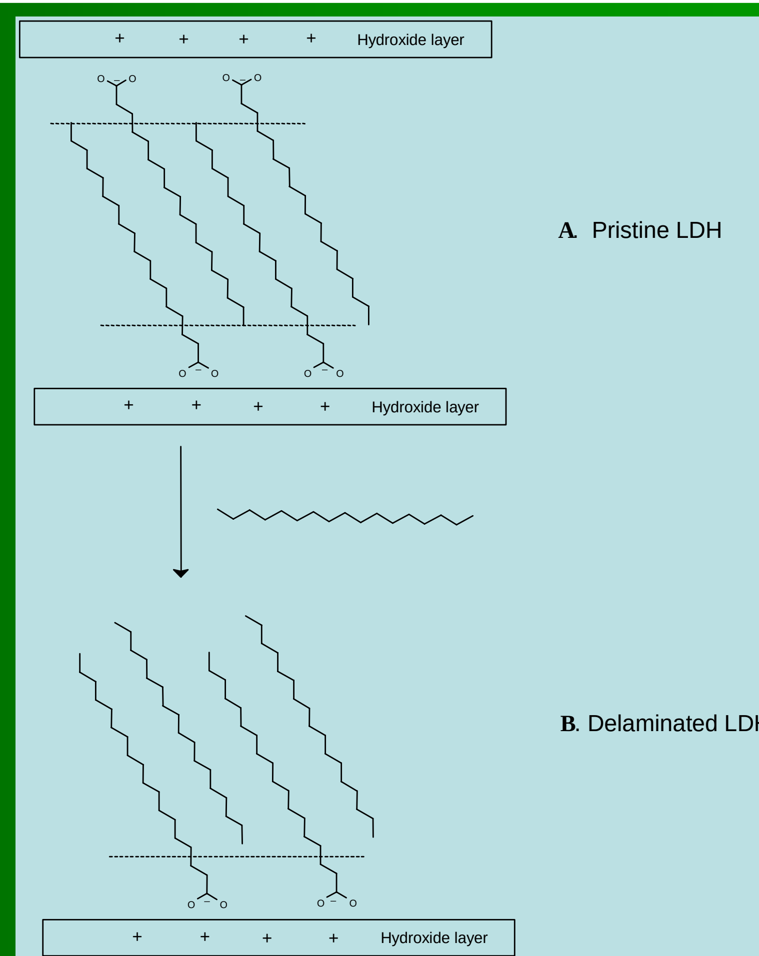
- Synthesis:
  - Mg Al versus Zn Al
  - Partial replacement of Mg with Ni
- Polymer incoroporation
  - Polystyrene 2:1 Mg-Al LDH-stearate : delamination in-situ
  - PVC with 2:1 Zn-Al LDH-CO_3 (probe thermal stability)
  - PET (blending results at 270 degrees C)

Polystyrene

- Layered double hydroxides (LDHs), also known as hydrotalcites or anionic exchanging clays, were synthesized in a stearate alkaline solution, followed by aging in n-hexadecane.

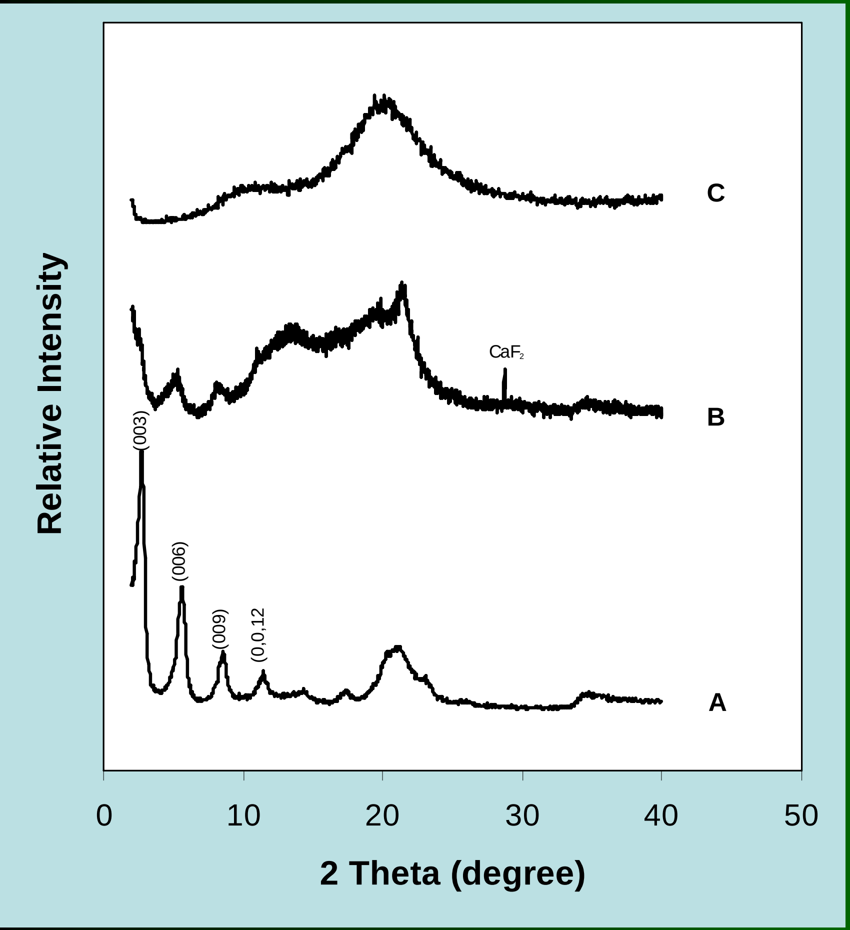
Mg-Al LDH + polystyrene





- FTIR confirmed the integrity of the individual LDH layers in this material, and showed uptake of n-hexadecane. Styrene was bulk polymerized in the presence of the delaminated LDH-stearate.

Mg-Al LDH + polystyrene



The aging gave a delaminated LDH material, as shown by x-ray diffraction (XRD).

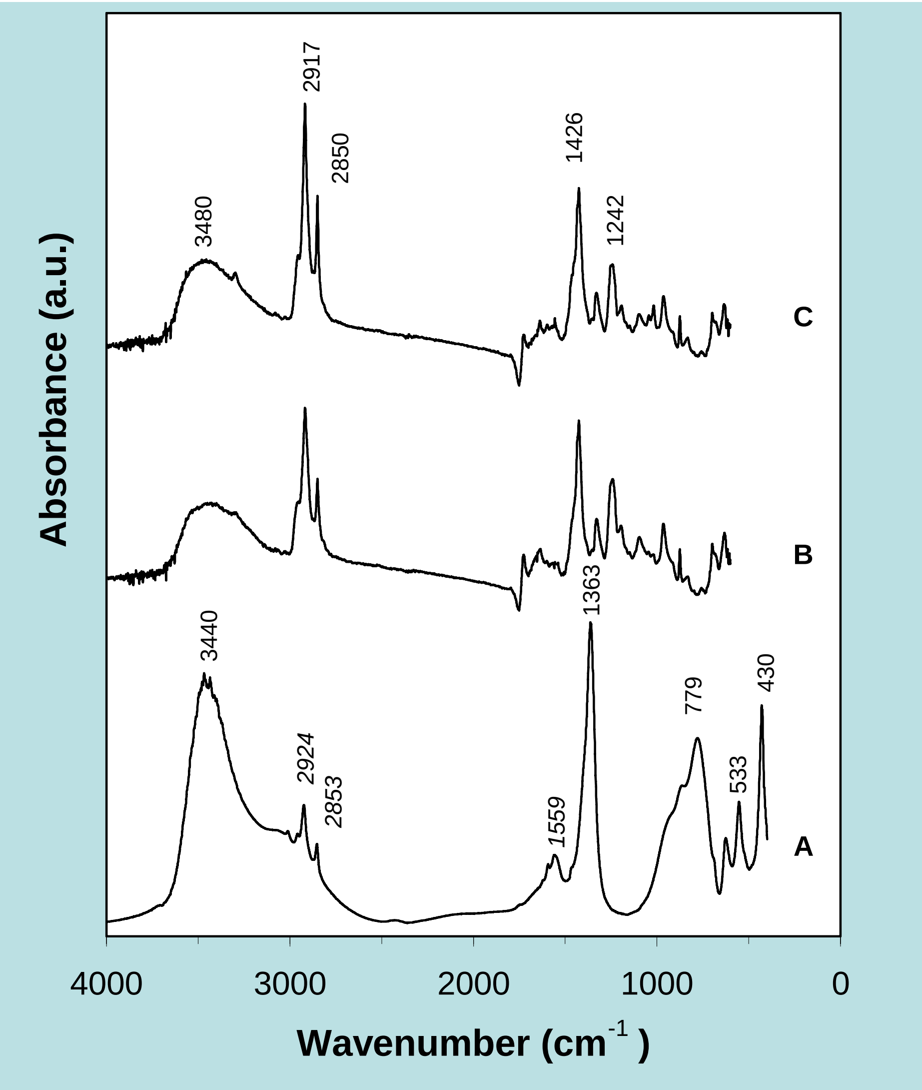
Zn-Al LDH Synthesis

- Zn2Al-LDH-CO3 coated with oleate (cis-CH3(CH2)7CH=CH(CH2)7COO-) was prepared as follows: 10 mmol of potassium oleate (8.0 g 40% paste, Aldrich), 50 mmol of Na2CO3 (Fisher Scientific, 99.8%) and 600 mmol of NaOH (31.4 mL 50% NaOH solution, Alfa Aesar) were dissolved in 18.2 Megohm Millipore deionized water (1.0 L) with gentle heating.
- Then a mixed salt solution containing 100 mmol of AlCl3.6H2O (24.14 g, Aldrich, 99%) and 200 mmol of ZnCl2 (27.20 g, Aldrich, 99%) was added slowly at room temperature to the above alkaline solution under vigorous stirring, and aged at 90-95 ^{o}C with stirring for 2 hours.
- After the mixture was cooled, precipitates were collected and thoroughly washed with deionized water via centrifugation, and then dried in an oven at 70 ^{o}C for 2 days.

PVC + LDH sample preparation

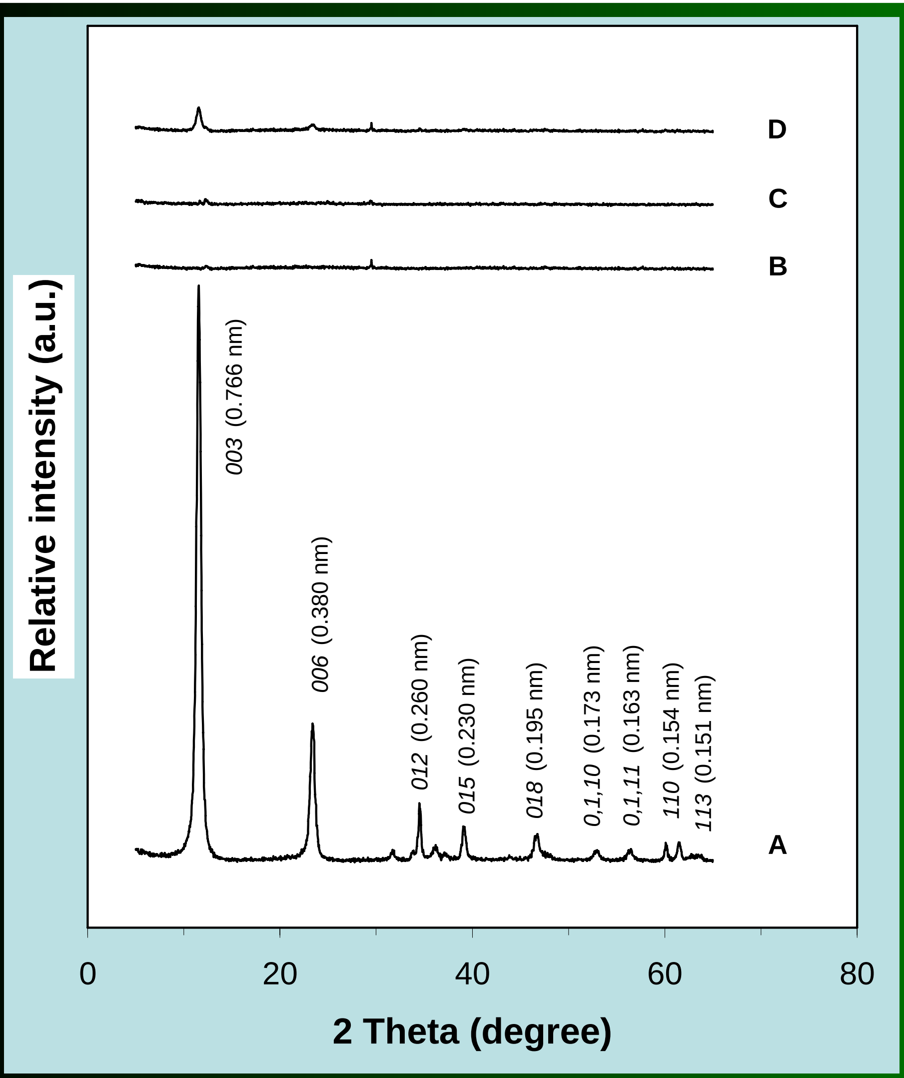
- An electrically heated and air-cooled 250 cc Brabender batch mixer with sigma blades was preheated to 180 ºC.
- Rigid poly(vinyl chloride) (PVC) pellets (240 grams, Geon 8700A natural) were added and fluxed at 30 rpm.
- Oleate-coated Zn2Al-CO3-LDH (10 grams) was gradually added, followed by continuous mixing for 2-3 minutes to ensure adequate mixing.
- The composite was removed from the mixing bowl and granulated. Ninety grams of granules were compressed and molded at 190 ºC into 50 mm × 50 mm × 4 mm plaques.

PVC + LDH: FTIR



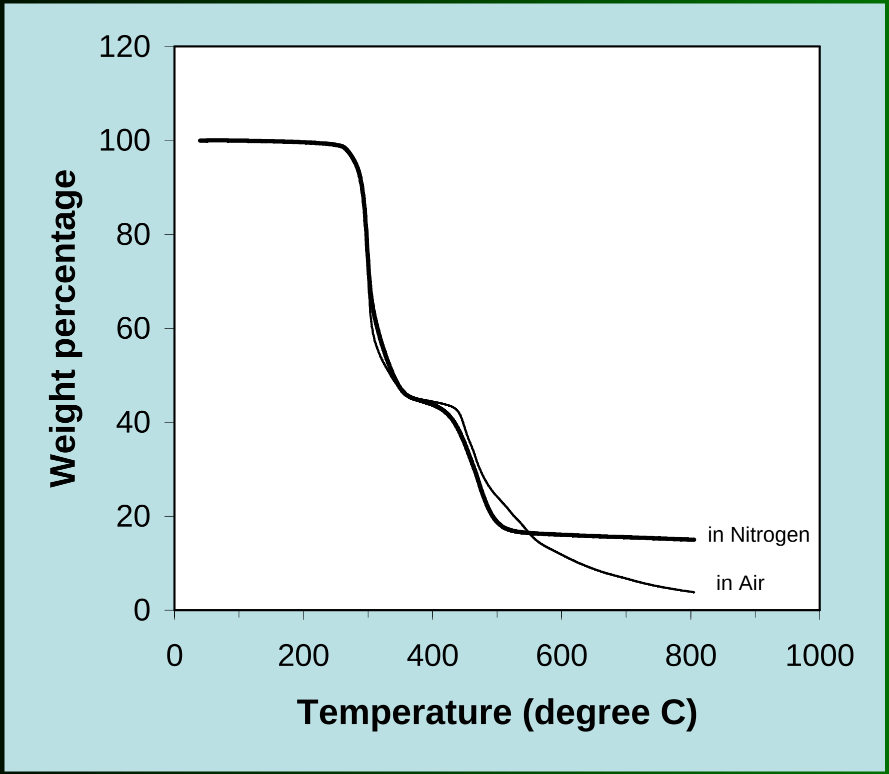
- Zn_2Al-LDH confirmed
- Oleate absorbed

PVC + LDH

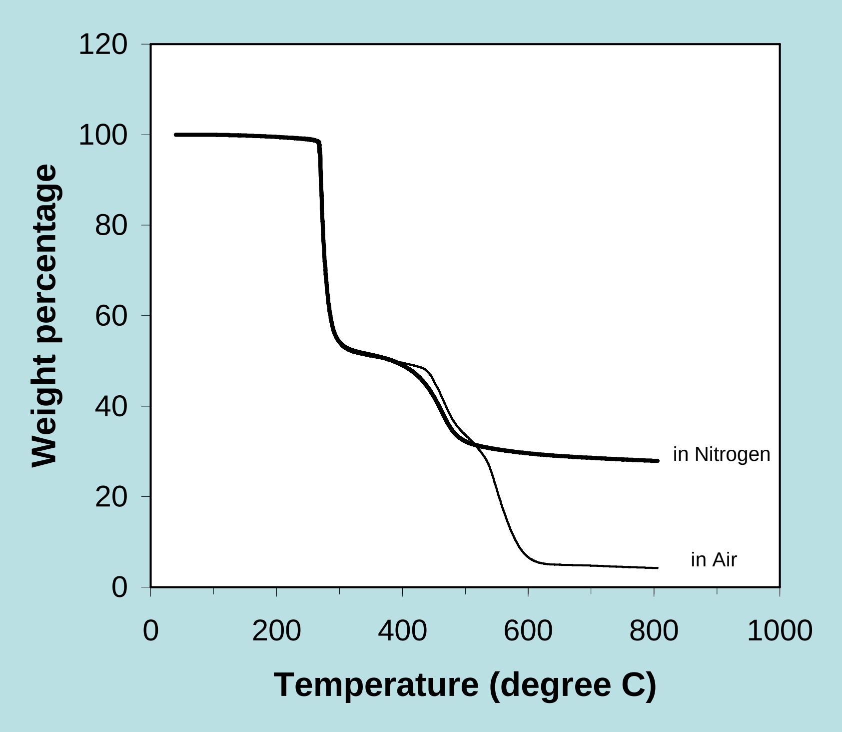


- LDH is carbonate strcutre
- Particle thickness of 30-40nm, corresponding to 40-50 hydroxide layers
- LDH in PVC is delaminated

PVC + LDH

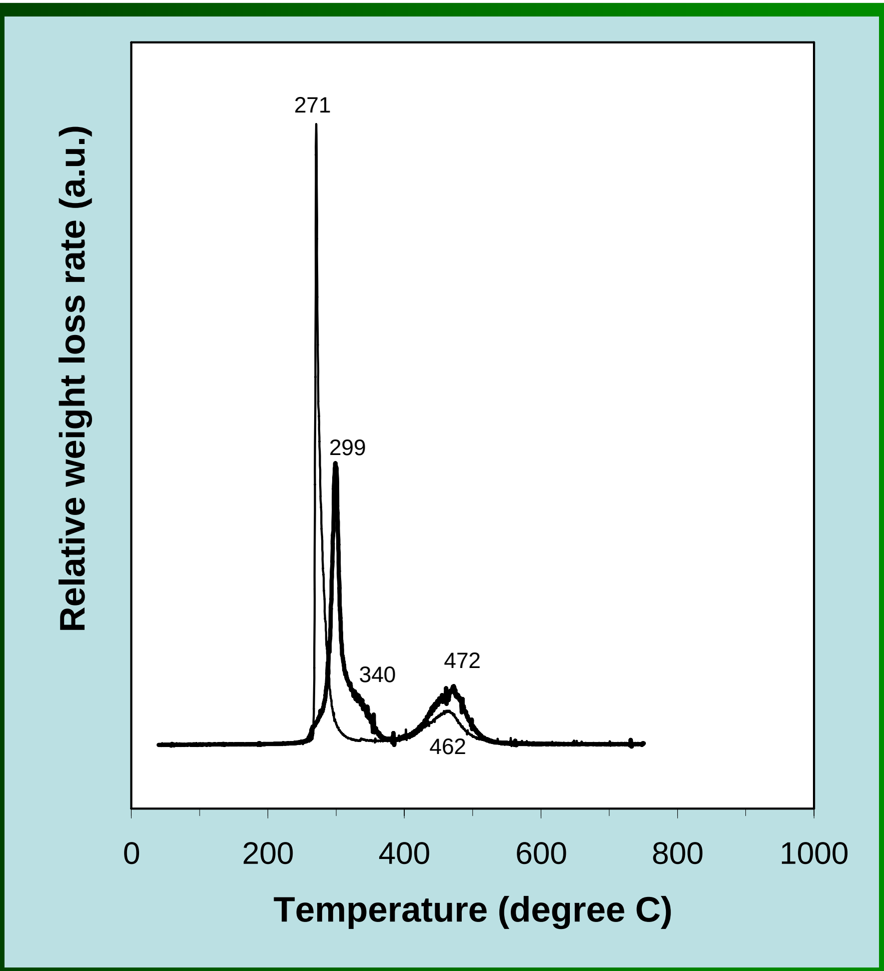


PVC



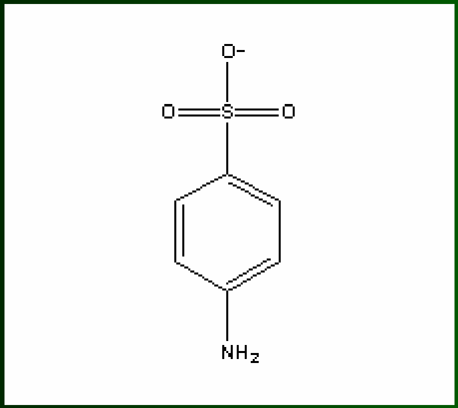
PVC + LDH

PVC + LDH : Weight loss



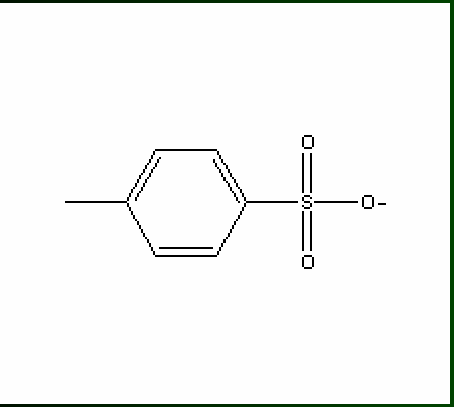
Synthetic strategies for LDH

LDH-sulfanilate

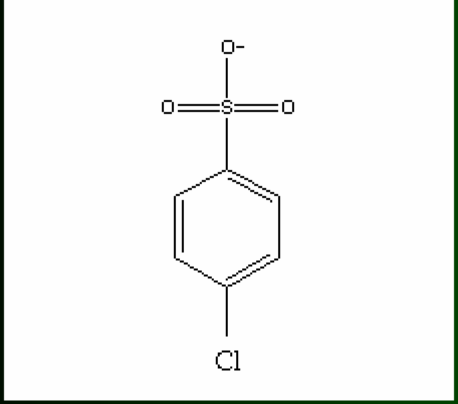


sulfanilate (p-aminobenzenesulfonate)

Ongoing efforts

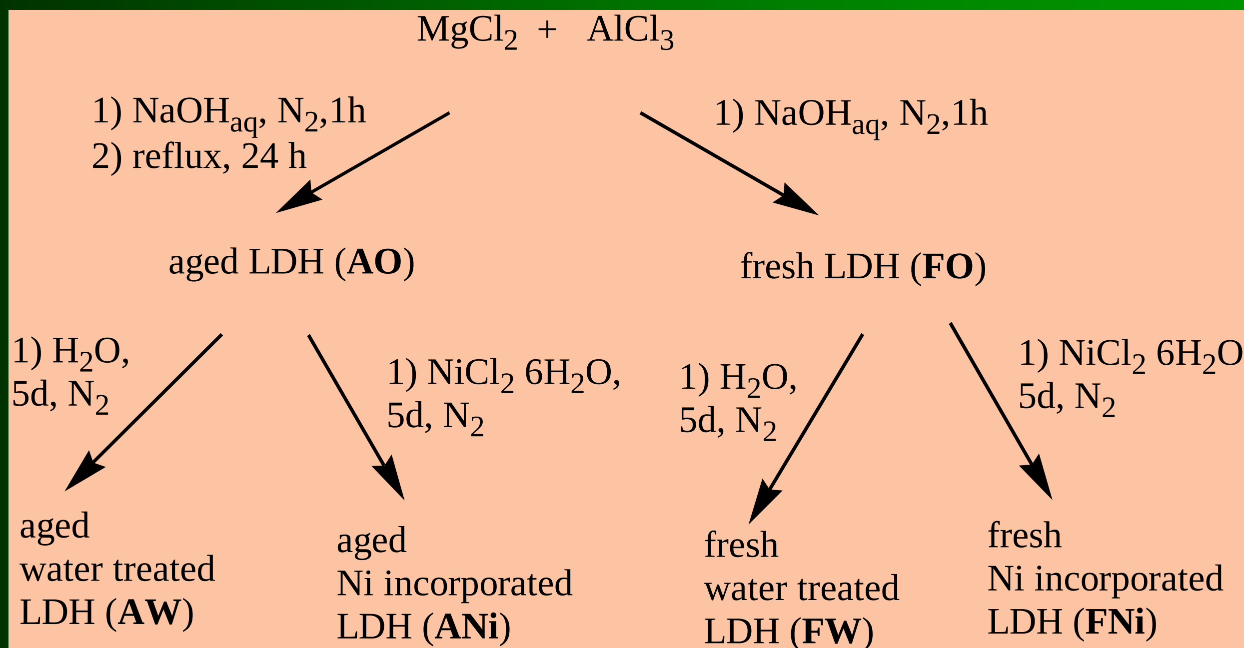


p-toluenesulfonate



p-chlorobenzenesulfonate

Incorporating Nickel



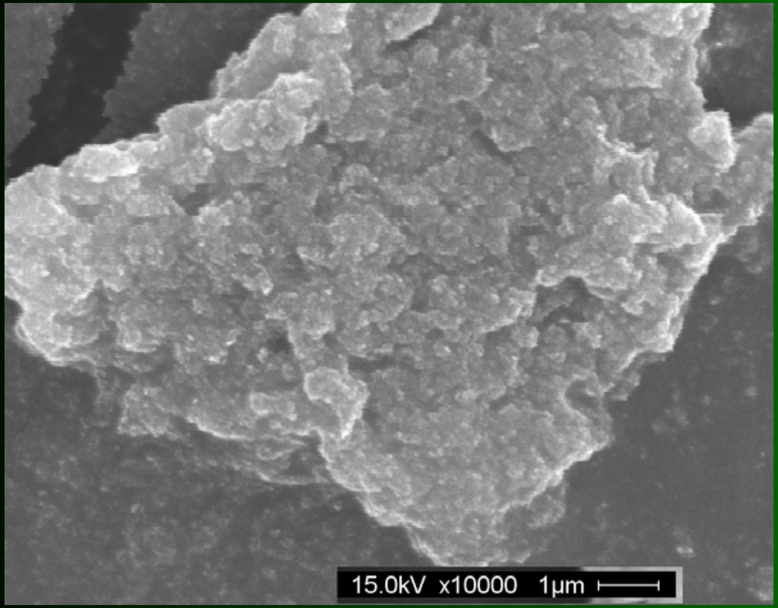
AAS

Table 1: Metals analysis for the nickel incorporated 2:1 Mg-Al LDH-Cl (FNi and ANi) by flame-AAS

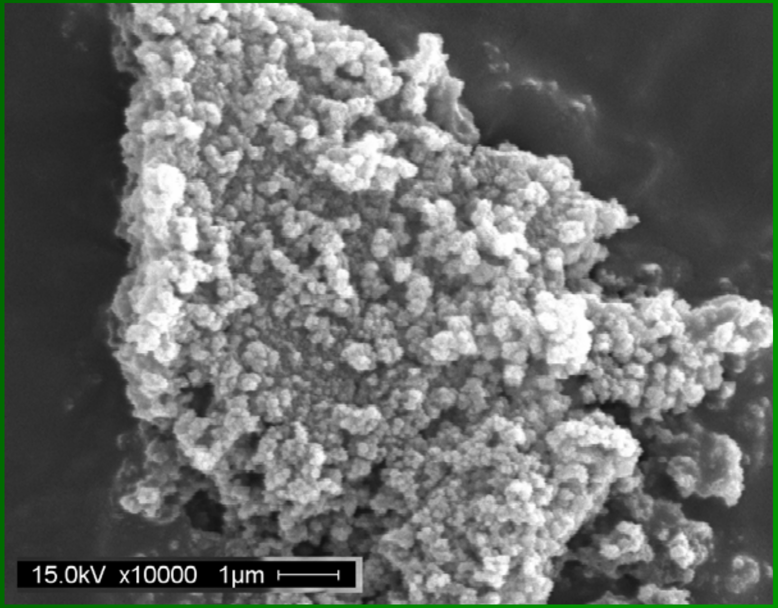
Material	%Mg	%Ni	%Al	Mg/Al	Mg/Ni	Ni/Al
Aged LDH[U1]	17.1	4.0	10.2	1.86	9.25	0.17
Fresh LDH	6.7	20.0	8.3	0.89	0.80	1.10

Nominal formulae:
Aged LDH[U2]: $Mg_{1.86}Ni_{0.18}$[U3]$Al(OH)_6Cl{\bullet}2H_2O$ = 256.32 g/mol
Fresh LDH: $Mg_{0.89}$ $Ni_{1.10}Al(OH)_6Cl{\bullet}2H_2O$ = 286.81 g/mol

SEM



Aged



Fresh

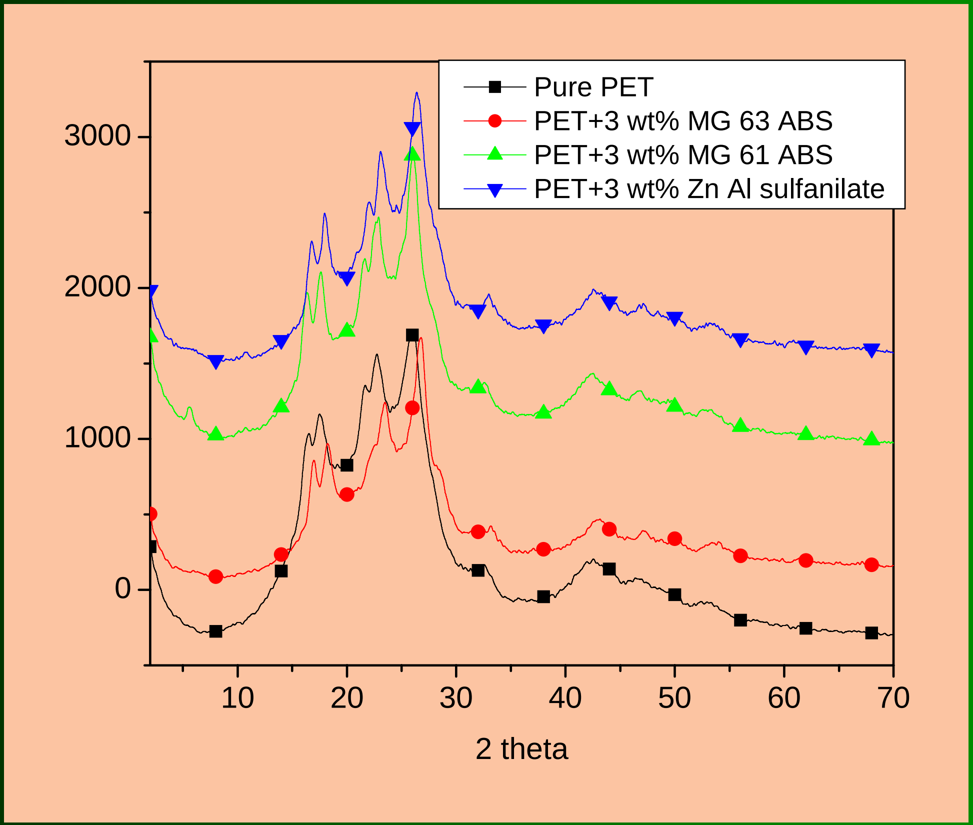
Blending with PET

- Challenges: Prior LDH compounding done at <200 degrees C with less surfactant degradation issues

Processing of PET-LDH

- LDH samples were grinded to make fine powder
- PET (Kosa 1101) pellets and LDH were dried for 36 hrs and 30 minutes respectively at 180 °C just before blending them to avoid any moisture in the sample
- Pellets and LDH were blended in twin screw mini extruder, Brbabender, USA Inc. at a speed of 80 RPM for 3-5 minutes at 270 °C.
- The blends were made into sheets using a Carver compression molding machine by applying pressure of 3 metric ton at 270 °C using the mold
- Pure PET was directly processed into the sheet

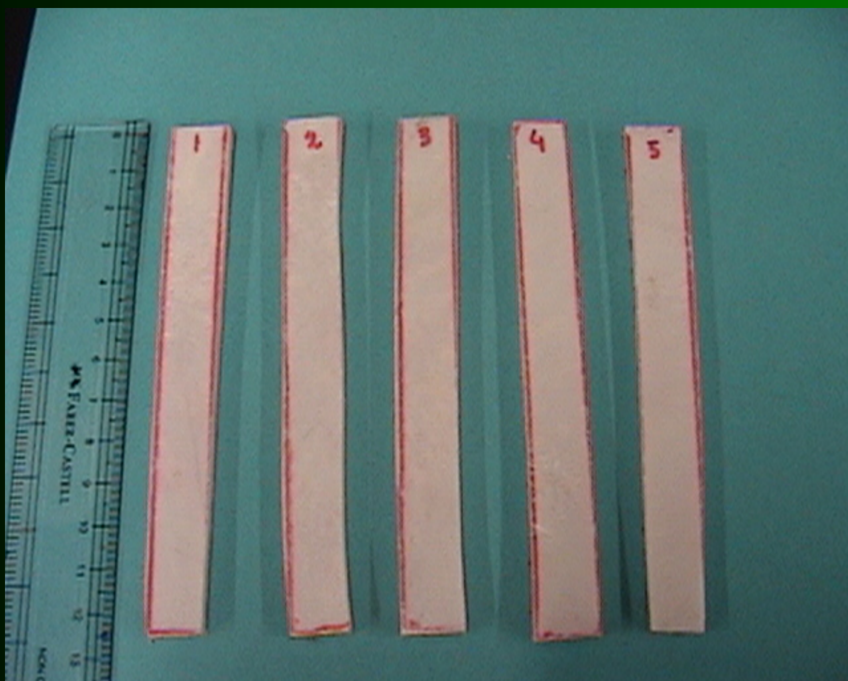
XRD



Pure PET
PET+3 wt% MG 63 ABS
PET+3 wt% MG 61 ABS
PET+3 wt% Zn Al sulfanilate
3000
2000
1000
0
10
20
30
40
50
60
70
2 theta

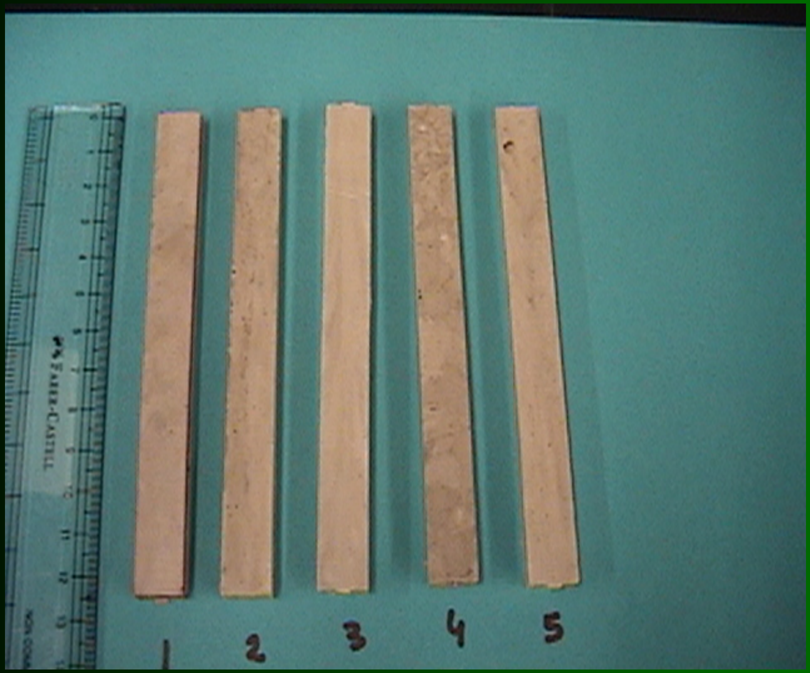
Image of mold and sheet

Images before and after flammability test for pure PET



PET+3 wt% MgAl-LDH

PET+3 wt% Zn Al LDH sulfanilate



UL-94 test results

Pure PET	t1(sec)	t2(sec)	t3(sec)	(t1+t2)(sec)
1	35	23	0	58
2	20	3	0	23
3	-	10.2	0	
4	20	22	0	42
5	12	23	0	35

PET+3 wt% MG 61 ABS	t1(sec)	t2(sec)	t3(sec)	(t1+t2)(sec)
1	13	5	0	18
2	15	3	0	18
3	13	0	0	13
4	15	5	0	20

PET+3 wt% Zn Al LDH sulfanilate	t1(sec)	t2(sec)	t3(sec)	(t1+t2)(sec)
1	14	2	0	16
2	12.9	-	0	
3	15	5	0	20
4	9	5	0	14
5	11	0	0	11

PET+5 wt% Mg Al LDH Sulfanilate	t1(sec)	t2(sec)	t3(sec)	(t1+t2)(sec)
1	11	0	0	11
2	27	0	0	27
3	17	0	0	17
4	12	2	0	14
5	15	3	0	18

PET+5 wt% Zn Al LDH CBS-Ni	t1(sec)	t2(sec)	t3(sec)	(t1+t2)(sec)
1	10	0	0	10
2	17	17	0	34
3	-		0	-
4	4	0	0	4
5			0	0
1	10	0	0	10
4	4	0	0	4

Summary of UL-94

Polymer	T1	T2	T1+ T2
PET	27	23	50
MgAl-LDH sulfanilate	13	4	17
ZnAl-LDH sulfanilate	13	4	17
PET+5 wt% Zn Al LDH CBS-Ni *	7	0	7

* Two samples did not reignite for T2

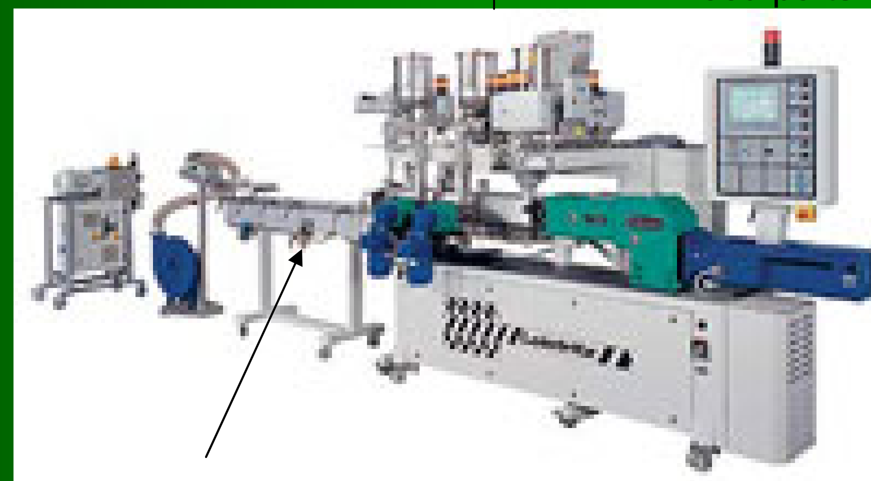
Summary

- LDH synthesis has been explored based on a range of metal cations and anions.
- Incorporation into PVC, polystyrene and PET has been conducted (blending and in-situ polymerization techniques)
- Stearate functionalization shows enhancement of dispersion via delaminated dispersions
- ZnAl-LDH coated with octanoate showed potential for 190 degrees extrusion processable LDH.
- Routes for Nickel incorporation into LDH were explored successfully
- Comparing MgAl, ZnAl, or NiAl sulfanilate was carried out using PET as a matrix.
- Increasing the processing temperature to 270 degrees C shows that high shear mixing technologies such as the Brabender require process optimization
- The processed materials demonstrated increased crystallinity in the PET
- U-94 test results indicated decreased times for all LDH modifed PET with the most improvement seen in the NiAl-LDH
- The LDH are functionalized to be compatible with PET, epoxy and polyurethane.
- Mechanical deformation effects of dispersion before and after burning are being investigated via nanoindentation.

Extrusion system

Extruder

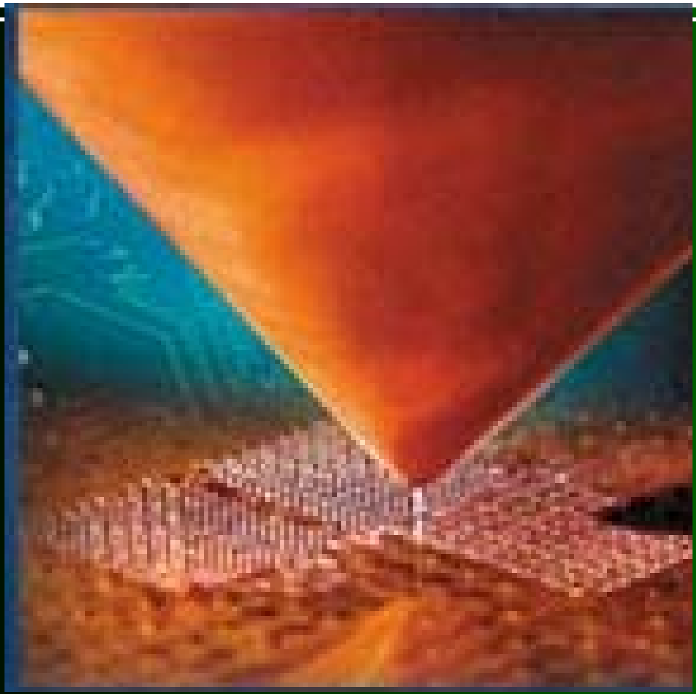
Multiple liquid/volumetric/gravimetric Feed ports



Connected to pelletizing unit

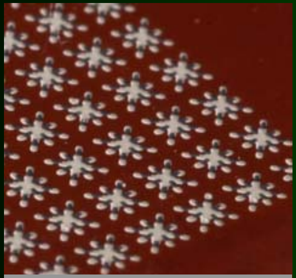
The extrusion system consists of a twin screw extruder and 4 ports located on the barrel to introduce thermally sensitive nanofillers into the polymer melt. A pelletizer is connected to a strand die via a water bath. Vacuum ports on the barrel ensure moisture sensitive polymer processability. A film/sheet die enables flexible substrate manufacture.

Maskless Mesoscale Materials Deposition (M^3D)

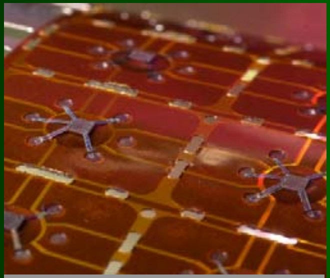


Versatile deposition system for metals, conductors, insulators, ferrites, polymers and biological materials on almost any substrate (silicon, glass, plastics, metals, ceramics)

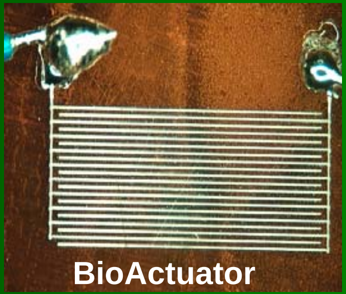
Ultrasonic vibrated solution is desposited by a CAD based technology and assisted by spray atomizers. The result is excellent dispersion of nanoparticles.



Resistor Pads

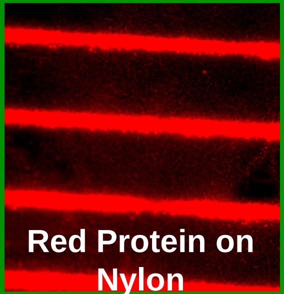


Smart Card



BioActuator

Cellular Growth



Red Protein on Nylon